were collected at 160 K with a Bruker AXS SMART CCD area-detector diffractometer on the high-flux single-crystal diffraction station 9.8 at CCLRC Daresbury Laboratory Synchrotron Radiation Source, with a wavelength of 0.6849 Å selected by a horizontally focusing silicon (111) monochromator and vertically focused by a cylindrically bent palladium-coated zerodur mirror.[13] The data set covered more than a hemisphere of reciprocal space with several series of exposures, each series with a different crystal orientation and each exposure taken over 0.2° rotation. Corrections were made for the decay of the synchrotron beam intensity as part of standard interframe scaling procedures.[14] The SSZ-23 sample was examined in the as-synthesized form and therefore included the template and charge-balancing fluoride ions. The crystal structure of SSZ-23 was solved with the direct methods program SHELXS-97[14] and refined with a full-matrix least-squares technique with the program SHELXL-97.[14] The final cycle of least-squares refinement included anisotropic displacement parameters for silicon, oxygen, carbon, and nitrogen atoms, and fractional occupancies for the fluorine atoms. The hydrogen atoms of the template molecule were placed in chemically sensible positions, and their positions were recalculated after each cycle of refinement. A total of 22014 integrated intensities were measured ($1.79 < \theta < 28.27°$), of which 8314 were unique and 4665 observed ($F^2 > 2\sigma(F^2)$). The large proportion of unobserved reflections is due to the small size of the crystal. Final refinement of the 571 least-squares parameters converged to $wR(F^2_{\mathrm{obs.}}) = 0.1657$, $wR(F^2_{\mathrm{all\ data}}) = 0.2028$, $R(F_{\mathrm{obs.}}) = 0.0811$, $S(F^2_{\mathrm{all\ data}}) = 0.992$; max. residual electron density $= 0.744\,\mathrm{e\,Å^{-3}}$. Refinement on F^2 was carried out against all data; the observed criterion $F^2 > 2\sigma(F^2)$ was used only for the calculation of $wR(F^2_{\mathrm{obs.}})$ and $R(F_{\mathrm{obs.}})$ and is not relevant to the choice of reflections for refinement. The final unit cell was refined to $a = 12.9594(3)$, $b = 21.7919(6)$, $c = 13.5980(4)$ Å, and $\beta = 101.855(2)°$, $V = 3758.3(2)$ Å at $T = 160$ K, space group $P2_1/n$, $\rho_{\mathrm{calcd}} = 2.13\,\mathrm{g\,cm^{-3}}$. Details of the final atomic coordinates, equivalent isotropic displacement parameters, and fluoride ion occupancies are given in Table 1. Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-408348.

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Formation of Isomeric Tetrathiotungstate Clusters $[\{\mathrm{Cp^*Ru(CO)}\}_2(\mathrm{WS_4})\{\mathrm{W(CO)_4}\}]$ by the Reaction of $[\mathrm{Cp^*_2Ru_2S_4}]$ with $[\mathrm{W(CO)_3(MeCN)_3}]$

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Dinuclear transition metal sulfur complexes of the type $[\mathrm{Cp^*_2M_2S_4}]$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$) are excellent starting materials for the formation of multinuclear transition metal sulfur clusters.[1] However, surprisingly little is known about reactivity of the iron-[2] or ruthenium-containing complexes.[3] In 1994 our group reported the reactions of $[\mathrm{Cp^*_2Fe_2S_4}]$ with iron and ruthenium carbonyl complexes to give *closo*-$[\mathrm{Cp^*_2(CO)_3Fe_2MS_2}]$ clusters (M = Fe, Ru).[2] Rauchfuss et al. reported that the ruthenium analogue $[\mathrm{Cp^*_2Ru_2S_4}]$[4] reacts with $[\mathrm{Cp^*Ru(MeCN)_3}](\mathrm{PF_6})$ and $[\mathrm{Cp^*Rh(MeCN)_3}](\mathrm{PF_6})_2$ to give $[\mathrm{Cp^*{}_3Ru_3S_4}](\mathrm{PF_6})$[3a] and $[\mathrm{Cp^*{}_3RhRu_2S_4(MeCN)}](\mathrm{PF_6})_2$,[3c] respectively. To examine whether this cluster construction methodology can be applied generally, the thermal reaction of $[\mathrm{Cp^*_2Ru_2S_4}]$ with $[\mathrm{W(CO)_3(MeCN)_3}]$ was investigated, and is described here. In the reaction, there was a dramatic redistribution of CO and S ligands between the W and Ru centers to give geometric isomers of tetrathiotungstate clusters $[\{\mathrm{Cp^*Ru(CO)}\}_2(\mathrm{WS_4})\{\mathrm{W(CO)_4}\}]$. Furthermore, we observed thermal and photochemical interconversion between the two isomers.

A solution of $[\mathrm{Cp^*_2Ru_2S_4}]$ in toluene was added to a solution of $[\mathrm{W(CO)_3(MeCN)_3}]$[5] (2 equiv) in acetonitrile (Scheme 1). The mixture was heated at 50 °C with stirring for 40 minutes. Evaporation of the volatile components and subsequent flash chromatographic separation of the residue over silica gel gave the two red-brown clusters **1** and **2** in 58% and 11% yield. Elemental analysis and mass spectrometry data indicated that **1** and **2** have the same formula $\mathrm{Cp^*_2Ru_2W_2S_4(CO)_6}$,[6] which is consistent with a cubane-type mixed metal–sulfur cluster $[(\mathrm{Cp^*Ru})_2\{\mathrm{W(CO)_3}\}_2(\mu_3\text{-}\mathrm{S})_4]$. However, X-ray diffraction study disclosed that this is not the case.[7] Cluster **1** was unequivocally determined to be $[\{\mathrm{Cp^*Ru(CO)}\}_2\{\mathrm{W}(\mu_3\text{-}\mathrm{S})_2(\mu_2\text{-}\mathrm{S})_2\}\{\mathrm{W(CO)_4}\}]$ (Figure 1). Interestingly, according to the crystal structure of **1**, redistribution of CO and S ligands

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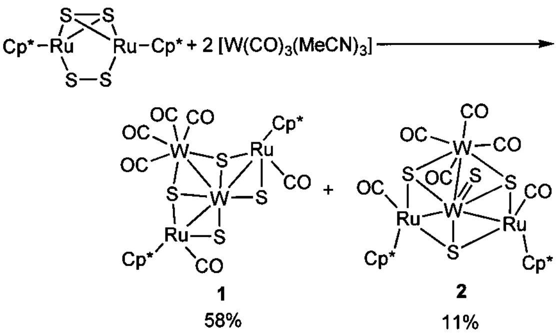

Scheme 1. Synthesis of **1** and **2** in toluene/acetonitrile (50 °C, 40 min).

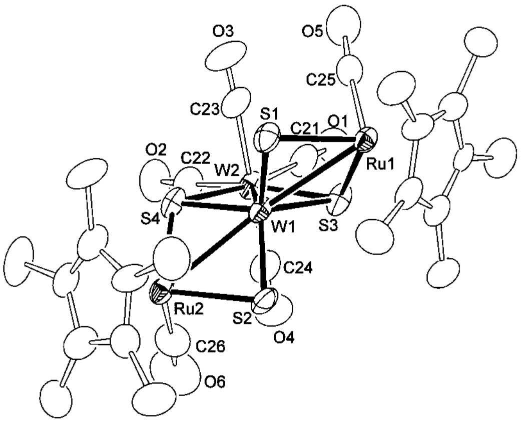

Figure 1. Structure of **1** (ellipsoids at the 50 % probability level). Selected bond lengths [Å] and angles [°]: W1–W2 2.9053(7), W1–Ru1 2.874(2), W1–Ru2 2.869(2), W1–S1 2.212(3), W1–S2 2.196(3), W1–S3 2.268(4), W1–S4 2.272(3), W2–S3 2.551(3), W2–S4 2.553(3), Ru1–S1 2.403(4), Ru1–S3 2.387(3), Ru2–S2 2.395(3), Ru2–S4 2.384(4), O3···O5 3.18(2), O4···O6 3.19(2); W2-W1-Ru1 98.82(3), W2-W1-Ru2 98.98(3), Ru1-W1-Ru2 162.08(4), S1-W1-S2 111.8(1), S1-W1-S3 106.5(1), S1-W1-S4 109.1(1), S2-W1-S3 107.6(1), S2-W1-S4 106.9(1), S3-W1-S4 115.0(1).

takes place between Ru and W centers without the loss of any ligands. The W1 atom, with four S ligands, adopts a slightly distorted tetrahedral geometry with S-W-S angles of 106.5(1) – 115.0(1)°. The WS_4 fragment is bound to one W atom by two S atoms and to two Ru atoms by four S atoms, two of which bridge one Ru and two W atoms in a μ_3 fashion; the other S atoms are bound to one Ru and one W atom in a μ_2 fashion. The Ru1 and Ru2 atoms each bear a Cp* and a CO ligand. The W2 atom, with four CO ligands and two S ligands, has a distorted octahedral geometry. The three metal–metal bond lengths (W1–W2 2.9053(7), W1–Ru1 2.874(2), and W1–Ru2 2.869(2) Å) lie in the normal range expected for metal–metal single bonds. The W–S bond lengths in $W^{VI}(=S)_4$ of 2.196(3) – 2.272(3) Å are similar to those in tetrathiotungstate clusters previously reported, and confirm the unsaturated bonding character. In contrast, the bonds of the two μ_3-S atoms (S3, S4) to the octahedral W2 atom (2.551(3), 2.553(3) Å) are 0.28 Å longer than those to the tetrahedral W1 atom. This reflects the dative bond character of the former bonds. The NMR spectroscopic data of **1** are consistent with the crystal structure (Figure 1).

The structure of $[\{Cp^*Ru(CO)\}_2\{W(\mu_3\text{-}S)_3(=S)\}\{W(CO)_4\}]$ (**2**) is shown in Figure 2. Redistribution of CO and S ligands between the Ru and W centers was again observed, without the loss of any ligands. Unlike **1**, **2** has a terminal S ligand. The WS_4 fragment is bound to one W atom by two S atoms and to two Ru atoms by three S atoms, two of which bridge one Ru and two W atoms in a μ_3 fashion; the third S atom is bound to two Ru atoms and one W atom also in a μ_3 fashion. Three metal–metal bonds (W1–W2 2.997(1), W1–Ru1 2.900(2), and W1–Ru2 2.892(2) Å) are somewhat longer than those in **1**. The elongation of the metal–metal bonds is attributable to the large steric repulsion between CO ligands on W2 and the two Ru atoms in **2** (O4···O5 3.07(3), O4···O6 3.09(3), and O5···O6 3.14(3) Å). All spectroscopic data indicate that the molecular structure of **2** in the crystal is maintained in solution.

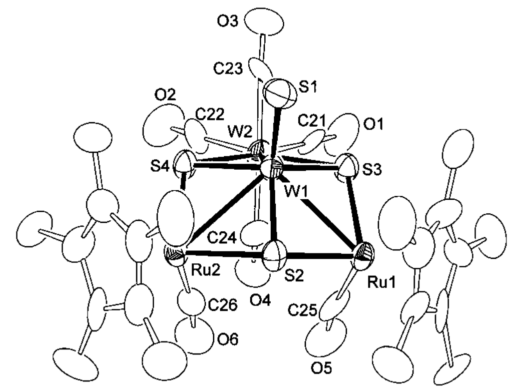

Figure 2. Structure of **2** (ellipsoids at the 50 % probability level). Selected bond lengths [Å] and angles [°]: W1–W2 2.997(1), W1–Ru1 2.900(2), W1–Ru2 2.892(2), W1–S1 2.125(7), W1–S2 2.261(6), W1–S3 2.274(6), W1–S4 2.276(5), W2–S3 2.558(6), W2–S4 2.566(6), Ru1–S2 2.394(6), Ru1–S3 2.421(6), Ru2–S2 2.373(6), Ru2–S4 2.408(6), O4···O5 3.07(3), O4···O6 3.09(3), O5···O6 3.14(3); W2-W1-Ru1 95.45(5), W2-W1-Ru2 95.69(5), Ru1-W1-Ru2 94.55(6), S1-W1-S2 109.9(2), S1-W1-S3 110.2(3), S1-W1-S4 110.4(3), S2-W1-S3 107.4(2), S2-W1-S4 106.8(2), S3-W1-S4 112.0(2).

Investigations of the reactivity of **1** and **2** revealed that isomerization between **1** and **2** occurred both thermally and photochemically in solution [Eq. (1)]. When a solution of **1** in

$$\mathbf{1} \underset{80^\circ C,\ 2h \quad ca.\ 90\%}{\overset{h\nu,\ RT,\ 1h \quad ca.\ 50\%}{\rightleftarrows}} \mathbf{2} \tag{1}$$

$[D_6]$benzene was irradiated, the amount of **1** decreased while the amount of **2** increased. Cluster **1** disappeared completely after one hour of irradiation, and **2** was formed in approximately 50 % yield with the deposition of an unidentified brown precipitate. Thermolysis of a solution of **2** in $[D_6]$benzene at 80 °C for two hours caused **2** to disappear completely to yield **1** in approximately 90 % yield. The difference in thermodynamic stability between **1** and **2** may be due to steric reasons: The steric crowding between CO ligands on W and the two Ru atoms is less severe in cluster **1** than in **2**.

The tetrathiometalates $[MS_4]^{2-}$ have been employed as building blocks for the synthesis of transition metal clusters for the last three decades. However, there are still few examples of $[MS_4]^{2-}$ coordinated to organometallic fragments.[8] Our system is the first example in which the $[MS_4]^{2-}$ unit combines with three organometallic moieties. The mechanism and general scope of application of this reaction are now under investigation.

Experimental Section

1 and **2**: A solution of $[Cp^*_2Ru_2S_4]$ (161 mg, 0.268 mmol) in toluene (15 mL) was added to a solution of $[W(CO)_3(MeCN)_3]$ in acetonitrile, which was prepared by refluxing a solution of $[W(CO)_6]$ (189 mg, 0.536 mmol) in acetonitrile (5 mL). The mixture was heated with stirring at 50 °C for 40 min. The volatile components were removed under reduced pressure, and the residue was extracted with toluene/hexane (1/1, 10 mL). Compounds **1** and **2** were obtained from the extracted solution and the insoluble material as follows: the extracted solution was subjected to flash column chromatography (silica gel, eluent toluene/hexane (1/1)). A red-brown fraction was concentrated to give **1** in 58% yield. An analytically pure sample was obtained by recrystallization from dichloromethane/hexane. The insoluble dark brown residue was dissolved in dichloromethane and subjected to flash column chromatography (silica gel, eluent dichloromethane). The red-brown fraction was collected, and the solution was concentrated to give red-brown **2** in 11% yield. Analytically pure **2** was obtained by recrystallization from toluene/hexane.

1: Elemental analysis calcd for $C_{26}H_{30}O_6Ru_2S_4W_2$: C 27.48, H 2.66; found C 27.83, H 2.74; MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): *m*/*z*: 1138 $[M^+]$; IR (KBr): $\tilde{\nu}_{max}$ [cm^{-1}] = 2031, 1975, 1959, 1921, 1848 $\nu_{(CO)}$; ^{1}H NMR ([D$_6$]benzene): $\delta = 1.68$ (s, 30H, Cp*); ^{13}C NMR ([D$_6$]benzene): $\delta = 207.8$, 204.3, 200.5 (CO), 100.5 (C_5Me$_5$), 10.2 (C$_5$*Me*$_5$); UV/Vis (toluene): λ_{max} [nm] (ε [cm^{-1}M^{-1}]) = 314 (1.7×10^4), 349 (1.5×10^4), 408 (1.2×10^4), 480 (sh), 535 (sh).

2: Elemental analysis calcd for $C_{26}H_{30}O_6Ru_2S_4W_2$: C 27.48, H 2.66; found C 27.71, H 2.95; MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): *m*/*z*: 1138 $[M^+]$; IR (KBr): $\tilde{\nu}_{max}$ [cm^{-1}] = 2019, 1975, 1905(sh), 1882 $\nu_{(CO)}$; ^{1}H NMR ([D$_6$]benzene): $\delta = 1.59$ (s, 30H, Cp*); ^{13}C NMR ([D$_2$]dichloromethane): $\delta = 209.7$, 208.1, 205.3, 196.2 (CO), 100.4 (C_5Me$_5$), 10.3 (C$_5$*Me*$_5$); UV/Vis (toluene): λ_{max} [nm] (ε [cm^{-1}M^{-1}]) = 325 (2.4×10^4), 429 (1.1×10^4), 510 (8.2×10^3), 682 (2.3×10^3).

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$[Re_5(\mu\text{-}H)_4(CO)_{20}]^-$ and $[Re_5(\mu\text{-}H)_5(CO)_{20}]$, Two Isolobal Analogues of Cyclopentane

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The $ReH(CO)_4$ fragment, isoelectronic with d^8 $M(CO)_4$, can be considered isolobal with (singlet) methylene,[1] as far as the formation of metal–metal interactions is concerned, since its frontier orbitals allow the interaction with two metal centers. The known $[ReH(CO)_4]_n$ oligomers ($n = 2$–4)[2] are therefore isolobal analogues of the corresponding $(CH_2)_n$ species: $[Re_2(\mu\text{-}H)_2(CO)_8]$ is an ethylene-like molecule,[2b] and the triangular and square-planar clusters $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ and $[Re_4(\mu\text{-}H)_4(CO)_{16}]$ "correspond" to cyclopropane and cyclobutane, respectively. Interestingly, until now no organometallic analogue of the most stable $(CH_2)_n$ oligomers (i.e., those with $n = 5$ or 6) was known. The pentanuclear cyclic clusters $[Re_5(\mu\text{-}H)_{5-n}(CO)_{20}]^{n-}$ ($n = 0$, 1) reported here fill this gap, at least partially.

We recently exploited the σ-donor capability of transition metal hydrides[3–5] in the synthesis of open-chain tri- and

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